Chapter 10
Effect of Natural Aging of Timber Building Structures on Fire Behavior and Fire Safety

Abstract This chapter presents the authors' original data on the effect of duration of natural (up to 700 years) aging of solid timber of different deciduous and coniferous species on fire safety characteristics and describes transformations in physical structure, chemical composition, and properties of timber species during natural aging of timber buildings and structures. It also presents experimental results of charring parameters and the properties of superficial char layers formed at fire action.

The chapter describes the process of biodegradation of timber species by timber-destroying fungi and the efficiency of complex bio-, moisture, and fire protection of constructional timber materials.

Over the whole period of genetic development of woody plants, transformation has occurred in external appearance, structure, and properties of wood substance as a result of millions of years of evolution. Various biotic and abiotic factors have played the defining role during formation of the feature complex of certain populations.

Historical age-class forms of wood substance may be nominally divided into three groups:

– Genetic age
– Biological age
– Service age

Genetic age, which defines the period of existence of a plant genus and species, has the longest retention of genotype signs, its main structural features and properties. During this age period, transformation of wood substance occurred at the genetic level under the impact of large-scale natural geographical and climatic changes, technical man-made disasters, etc.

Biological age corresponds to the period of sprouting and life of certain plants under certain soil and climatic conditions.

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For example, Siberian larch trees that reached the age of 500 or more years were found on hillsides of the Altai–Sayan Mountains, in spite of soil moisture deficit and cold weather conditions within the summer plant growth period.

Service age is characterized by the period of using timber of already-cut trees as individual products or members of timber building structures, finishing and lining materials under various usage conditions until they reach a certain marginal capability state. It is fair to expect that the biological age of cut trees and their condition will affect the service life and lifetime of timber building structures, all other usage conditions being equal.

This chapter deals with the problem of durability of timber as a constructional material and effect of its aging during the use under natural climatic conditions on the transformation in structure, chemical composition, and properties, including fire behavior.

The interest in old timber structures in particular is quite understandable, both from the point of view of studying the natural timber aging process and preservation and restoration of historical wooden architectural monuments.

10.1 Transformations in Physical Structure, Chemical Composition, and Properties of Constructional Members in Old and Ancient Timber Buildings

Eight climatic zones are distinguished on our planet, according to the relative importance of climatic parameters and combinations thereof: temperature, humidity, elevation above sea level, proximity of seas, proximity of industrial zones, and other meteorological conditions (solar radiation, atmospheric precipitation, pressure, fog, cloudiness, snow cover, wind). These zones are as follows: equatorial, subtropical, tropical, monsoonal, Mediterranean, oceanic, continental, and polar.

Russian territory has regions with cold and moderate climates. Regions with very cold and cold continental climates (Yakutia, Salekhard), arctic subpolar, eastern and western (Tiksi, Dickson Island), moderately cold (Tyumen), moderate (Moscow, Murmansk), subhumid (Vladivostok), and humid temperate climates (Novorossiysk) are distinguished, respectively. The most representative points of each climatic region are shown in brackets (GOST 16350-80).

A wide combination of various factors affects the durability of timber buildings and structures in a given climatic region. As with synthetic polymers (Emmanuel and Buchachenko 1982; Popov et al. 1987), the most essential physicochemical changes during the use of timber structures result from photochemical, hydrolytic, and thermal oxidative destruction; the effect of mechanical stresses; and other types of destructive processes.

Unfortunately, until now, no clear-cut effect of the conditions and duration of natural aging of timber on the interrelation of transformations in structure and chemical composition with many properties of the material has been established.

There is almost no information on the effect of natural aging of timber building structures on fire behavior and fire safety.

The process of natural aging of timber structures is different for different timber species and usage conditions. It does not lend itself well to a simple description and forecasting. The main reason for difficulties in studying the timber aging process is the complexity of the object itself, the diversity of its usage conditions, and the variability of its mechanical and physicochemical properties.

It becomes clear why the scarce results of studying the timber aging are often largely contradictory.

It is worth emphasizing that the studies of the natural aging of timber are aimed mainly on the analysis of change dynamics in macroscopic characteristics of timber structure and properties during long-term usage. However, the true process of timber aging, the mechanism and kinetics, limiting stages, and also the possibilities of effectively regulating or its slowing have not been examined. Solving this problem requires creating new approaches and methods, considerable collaborative efforts of the scientific community.

The duration and service life of timber buildings and structures, if properly used and promptly repaired, may reach many hundreds of years. Unique examples of long-term preservation of timber buildings and structures are Church of the Transfiguration on Kizhi Island (1714); the Church of the Resurrection (1776) and the eighteenth-century Spaso-Preobrazhensky Church in Suzdal; Voznesenskaya cube church in the village of Kushereka, Onezhsky region (1669); and the eighteenth-century Saviour's Church in the village of Fominskoye, Kostroma, among others (Kisternaya and Kozlov 2007; Varfolomeyev et al. 1990; Isayeva and Bryukhanova 1969; Pischik et al. 1971; Pokrovskaya 2003).

The significant enhancement of the strength characteristics of larch timber during its long-term use from the fifth–ninth centuries to the present as a material for shoring the foundations of various buildings in Venice is truly phenomenal. There are examples of unique preservation of larch timber for 1,800 years (Trajan's bridge piles over the Danube) (Isayeva and Bryukhanova 1969). This shows the very high resistance of larch timber to failure. A law allowing larch to be used for public construction only, i.e., bridges, mills, and dams, but mostly in shipbuilding existed in Russia up to 1858.

The internal constructional members of the Moscow Kremlin Cathedrals, Saint Basil's Cathedral, the Winter Palace in St. Petersburg, and some other historical monuments in Russia were made of larch (Isayeva and Bryukhanova 1969).

In the past, pine and fir were the main material for construction of nearly all timber residential and commercial buildings and structures as well as of the majority of religious buildings in Russia.

The studies carried out to date are the evidence that essential physicochemical changes occur in timber during long-term usage under natural conditions (Kisternaya and Kozlov 2007; Varfolomeyev et al. 1990; Isayeva and Bryukhanova 1969; Pischik et al. 1971).

The research paper (Isayeva and Bryukhanova 1969) established that the mechanical properties of larch from a timber house built in Krasnoyarsk deteriorated

noticeably in 230 years of natural aging under the climatic conditions of Siberia compared to present-day timber. Samples for analysis were taken from the undamaged part of a lower row of logs of the building. Erosion was recorded only in the surface layer of the logs 2–3 cm thick. On average, the density of the larch samples decreased by 8 % (to 585 kg/m^3); compressive strength along the grain, by 15 % (to 45.3 MPa); bending strength in the tangential plane, by 29 % (to 68.1 MPa); and in splitting parallel to the grain in the same plane, by 28 % (to 6.1 MPa). Anatomic analysis of tangential shears of old timber showed degradation of tracheids at their junction points and heartwood ray cells. The authors (Isayeva and Bryukhanova 1969) consider formation of large in-plane tensile stresses in the tangential direction during periodic drying of the logs to air-dry condition to be the reason for this degradation.

The changes in pine timber density, ρ_{12}, static bending strength in the tangential direction and compression along the grain (Varfolomeyev et al. 1990) were identified in timber architectural objects of Arkhangelsk Region that had been standing from 85 to 351 years. Samples were taken from sound clean timber.

Chemical composition analysis was performed for outwardly undamaged external surface layers 2–4 mm thick.

A nonlinear change in pine timber density is observed in the aging process: a reduction from 490 to 420–430 kg/m^3 in 140 and 199 years and a later increase to 565 kg/m^3 (Fig. 10.1). Strength properties are changed almost synchronously. In addition, their variation decreased from 10–12 to 3–4 %, indicating stabilization of timber state over long-term usage of constructional members under load.

Long-term external effects of atmospheric oxygen, solar radiation, wind, precipitation, and increased air temperature on timber result in destructive chemical reactions, primarily in the carbohydrate part of the material. In addition, hemicelluloses, which have a low degree of polymerization compared to cellulose, are especially vulnerable (Table 10.1). The content of main components of pine timber is expressed in % relative to an absolutely dry sample.

The data of Table 10.1 lead to the conclusion that the most significant reduction of carbohydrates in the chemical composition occurs in external constructions under direct influence of the atmospheric environment. It is especially noticeable in the timber of church crosses. Reduction in the content of extractives and an increase in lignin content are observed simultaneously with decomposition of cellulose and hemicelluloses. A rapid change in the extractives content occurs within the first 100 years of aging. This situation is explained by washout and evaporation of extractives (lightly volatile terpenes) from the surface layers of logs at higher summer temperatures. Destructive processes slow down indoors and when logs are protected with a board lining against direct moisturizing and solar radiation.

Changes observed in the chemical composition of pine timber under various usage conditions of building structures point to the important role of photo oxidation and hydrolytic reactions in the general natural aging process of the material.

Data on the behavior of timber construction made of deciduous species under natural aging conditions are very sparse.

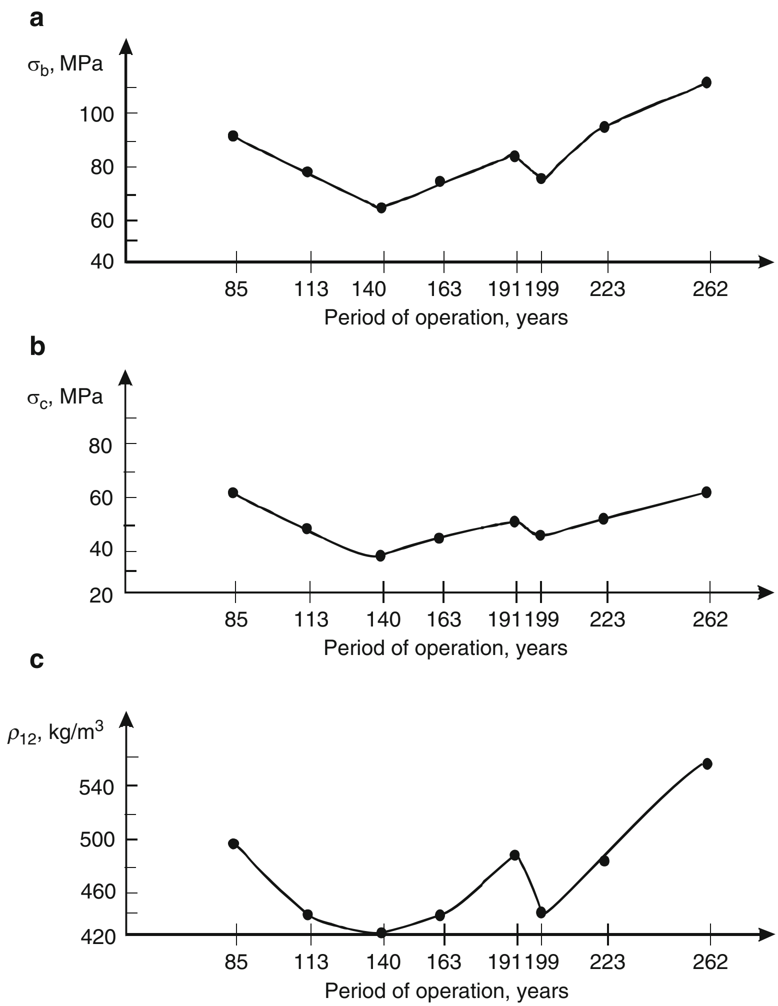

Fig. 10.1 Effect of duration of natural timber aging on bending strength (**a**), compressive strength (**b**), and density ρ_{12} (**c**)

In the 1970s, a group of scientists studied the chemical composition of old and present-day timber of two species: fir and maple (Pischik et al. 1971). The present-day fir samples were obtained from Neysky Timber Mill (Neya, Kostroma Region); fir samples with 50–70 years of usage were taken from demolished buildings in Cherkizovo (Moscow); fir samples with 200 years of usage were from a disassembled ancient monument in Textilshchiki (Moscow); and fir samples with 150–200, 300–400, and 400–700 years of usage were obtained during restoration of various churches in Riga. The present-day maple wood samples were delivered from a timber mill in Apsheronsk, Krasnodar Territory; samples with 60–70 years of

Table 10.1 Effect of the duration of natural aging on the chemical composition of different constructional members of timber structures

Length of usage, years	Constructional member and usage conditions	Lignin, %	Cellulose, %	Easy hydrolysable polysaccharides, %	Extractives, %	Ash content, %
0	–	26.5	54.3	17.8	10.7	–
85	Floor joist in a room	25.3	55.7	16.4	4.9	0.34
113	Cornice detail- external structure	28.2	48.9	14.8	2.2	0.34
124	Upper wall crown under board lining	28.7	49.9	16.7	2.1	0.25
124	Same	26.2	51.6	17.2	3.0	0.74
191	Pole ladder under roof	28.8	50.0	13.7	2.0	1.97
199	Internal structure member	27.9	48.9	16.8	4.6	0.67
223	Upper wall crown under board lining	27.3	50.5	14.4	4.9	0.29
262	Rafter member	26.8	50.9	14.7	3.6	0.18
262	Church cross	29.6	48.5	9.8	0.8	0.89
351	Floor joist in compartment	26.4	51.9	16.7	3.6	0.37

Table 10.2 Change in chemical composition of fir and maple timber in the process of long-term natural aging

Timber	Content in timber, %				
	Ash	Extractives	Cellulose	Lignin	Easily hydrolysable substances
Present-day fir	0.26	3.96	54.47	26.29	17.76
3-year-old fir	0.28	7.5	54.40	25.40	18.50
50–70-year-old fir	0.25	7.28	53.97	25.01	17.80
100–200-year-old fir	0.48	10.63	50.78	24.64	14.16
200-year-old fir	0.24	10.57	51.72	26.12	13.34
200–300-year-old fir	0.48	11.3	52.34	24.90	13.16
300–400-year-old fir	0.47	15.22	50.77	24.26	12.11
400-year-old fir	0.39	13.18	52.78	25.03	12.36
500–700-year-old fir	0.42	21.36	49.45	23.97	10.35
Present-day maple	0.56	8.19	46.53	24.18	22.51
3-year-old maple	0.39	7.59	45.99	24.60	22.79
70-year-old maple	0.51	8.83	46.53	23.97	19.80
100-year-old maple	0.52	7.3	47.71	21.91	18.98

usage were obtained from Sweden. Maple 100 years old was obtained from Moscow Region. The results of chemical analysis of the samples are presented in Table 10.2 (Pischik et al. 1971).

Data analysis leads to the conclusion that easily hydrolysable hemicelluloses suffer the greatest destruction during natural aging. Their content after 700 years of aging of fir timber building constructions is reduced by 8 absolute % or 44 % relative to the initial concentration.

When fir and maple samples with 100 years of usage are compared, the relative reduction of hemicelluloses is 22.5 % in fir timber and 15.7 % in maple. Cellulose and lignin are less changeable. The relative reduction of cellulose concentration in fir is about 9 % in 700 years. The observed tendency of simultaneous reduction in cellulose and lignin content in fir timber during aging suggests minor participation of white rot fungi in the destructive process. Lignin is the most hydrolytically and thermally resistant component of timber.

Figure 10.2 shows the content of main chemical components of coniferous timber in timber architectural monuments as a function of usage time (Pokrovskaya 2003). The nonlinear character of change in cellulose and lignin content can be seen by year built. The minimum lignin content corresponds to the maximum increase in cellulose. In addition, a steady decrease in pentosan concentration with an increase in service age of the timber can be traced.

Data on the properties of ancient archaeological timber of building structures are extremely interesting.

The research paper (Kazanskaya et al. 1975) studies the chemical composition of elements of timber building structures of the tenth–thirteenth centuries found during archaeological digs in Novgorod and Brest (Table 10.3).

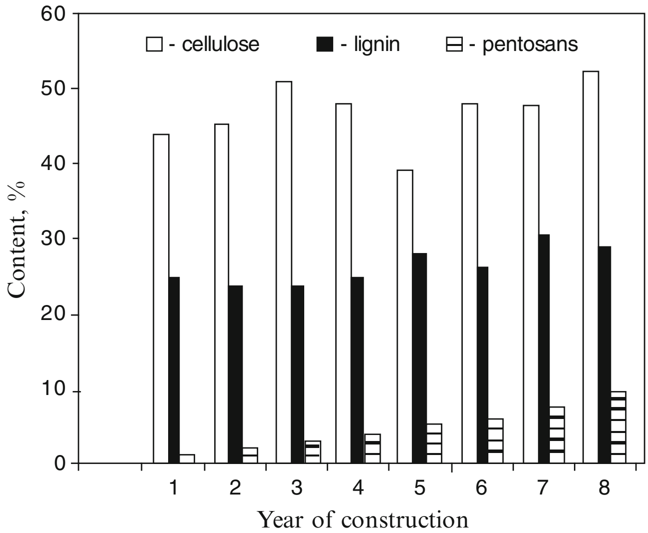

Fig. 10.2 Content of components of coniferous timber in timber architectural monuments: *1* year 1493, *2* year 1600, *3* year 1699, *4* year 1700, *5* year 1750, *6* year 1790, *7* year 1870, *8* year 2000

Table 10.3 Chemical composition of timber of the tenth–thirteenth centuries

	Timber species		
Components, % of absolutely dry timber	Ash tree	Birch	Pine
Ashy substances	6.29	2.71/0.14	7.88/0.17
Substances extractable with cold water	6.20	4.94	3.93
Substances extractable with water at 90 °C	7.60	5.42/1.41	5.14/3.19
Substances extractable with an alcohol–benzene mixture	2.88	3.82	4.88
Lignin	51.69	46.71/19.74	44.97/24.68
Cellulose	14.53	16.49/35.38	31.53/44.10
Pentosans	17.93	15.13/24.57	6.36/7.60
Easily hydrolysable polysaccharides	18.52	16.95/26.54	11.62/17.84
Low-hydrolysable polysaccharides	15.48	18.16/39.40	33.21/47.66

Note: The content of components of present-day timber is given in the denominator

From the foregoing data, it follows that the content of cellulose and other polysaccharides in archaeological timber is significantly reduced compared to present-day samples. The content of pentosans in deciduous wood changes the most. Lignin content almost doubles. The high percentage of ashy substances in archaeological timber may be due to the adsorption of metal-containing substances from the soil over a very long period.

Timber density (volume weight) is the main indicator of the macrostructure of the material. As shown above, many physical and mechanical properties of timber are

closely interconnected with its density (Chap. 2). When timber ages under natural conditions, its density changes nonlinearly with age.

According to (Pischik 2005), a timber density corresponds to each age (biological and service). In the author's opinion, the density and properties of a particular timber species as aging progresses change cyclically according to a single law. The number of annual growth layers in a growing tree and timber destruction during aging are interrelated cyclic processes based on double centennial cycles of solar activity.

These cycles leave their marks on the year-ring analysis scale of woody plants.

The cycle duration is 200 years for coniferous species and 260 years for deciduous species. Graphically, each cycle has the form of an inverted bell and consists of two symmetrical branches: descending and ascending. On a descending branch, density decreases as a result of mass reduction during carryover of destruction products and preservation of specific volume, the timber becomes lighter, and absolute factors of the properties decrease. On an ascending branch, density increases due to shrinkage and irreversible volume contraction, the timber becomes darker, and absolute factors of the majority of properties increase. The author (Pischik 2005) associates the destructive aging processes with hydrolysis and thermal oxidation reactions of timber components. Shrinkage processes are associated with lignin condensation reactions and consolidation of the remaining components. The Fourier equation for harmonic vibrations has been proposed to describe the cyclic dependence of density and other properties of timber on its age (Pischik 2005; Pischik and Vikhrov 1996):

$$y = a_0 + a_1 \cos \tau + b_1 \sin \tau,$$

where y is the observed factor; τ is the year of timber cutting; and a_0, a_1, and b_1 are the constants.

Pine timber density is changed with age according to the equation:

$$\rho = 0.5–0.9 \cos (0.03\tau - 1,339) – 0.16 \sin (0.03\tau - 1,339)\, , \mathrm{g/cm}^3.$$

This dependence is suitable for all coniferous species and can serve as a scale for determining the age of the material. A similar approach has been implemented for deciduous species. A way of determining timber age has been proposed based on these scales and the involvement of nondestructive inspection methods for timber product properties. The accuracy of estimating timber age of historical and cultural works (icons, picture frames, parts of musical instruments) is ±15 years.

However, it should be noted that if two parallel and competing processes – degradation and cross-bonding of macromolecules – occur during material aging, then the dependence of any property on time may be described by an equation of the form of (Emmanuel and Buchachenko 1982):

$$y = a \exp (-k_1 \tau) - b \exp (-k_2 \tau) + y_0,$$

where k_1 and k_2 are the rate constants for degradation and cross-bonding reactions and a, b, y_0 are the constants.

If under aging conditions $k_1 < k_2$, factor $y(\tau)$ will pass through a minimum. However, under operating conditions, it may turn out that $k_1 > k_2$ and then dependence $y(\tau)$ will have a maximum (Emmanuel and Buchachenko 1982).

Within one cycle of global influence of solar activity on timber aging, one might expect the influence of shorter cyclic climatic effects on this process.

A study of the kinetics of various chemical reactions in timber during aging provides ways for clarifying the mechanism of this process.

Natural aging of timber building structures occurs under the effect of mechanical stresses.

The kinetic theory of the durability of polymeric materials is based on thermofluctuation mechanism of their molecular destruction. Mechanical destruction of polymers is regarded as thermal destruction activated by mechanical stress. The activation energy of mechanical destruction U_0 in the famous Zhurkov equation for durability of material τ under load σ:

$$\tau = \tau_0 \exp\left[(U_0 - \gamma\sigma)/\mathrm{RT}\right]$$

for many polymers coincides with the activation energy of thermal destruction (Regel et al. 1974). In the equation, value γ reflects the probability of accidental statistical disintegration of the main bonds of a macromolecular chain.

Under mechanical loading of solid bodies, the observed deformation primarily affects amorphous regions with the least order of packing of macromolecules, local clustering of structure defects, and strained bonds. Breakdown of these bonds is not accidental (value γ is small); it is the source of consecutive formation of submicrocracks and microcracks and generates the formation of main cracks, growing cracks, and failure of the solid body (Regel et al. 1974).

Later works (Popov et al. 1987) established that tensile load accelerates the process of photooxidation of polymeric materials. In the presence of moisture (in air or in an inert medium), it also accelerates the hydrolysis of heterochain polymers. The double effect of the load on hydrolysis of heterochain polymer PA-6 – linear reduction of activation energy E_0 and reduction of pre-exponential factor k_0 of the reaction of amide bond hydrolysis with increasing load – has been successfully revealed. Reduction of pre-exponential factor k_0 in the equation:

$$k = k_0 \exp\left[-\left(E_0 - \alpha'\sigma/\mathrm{RT}\right)\right]$$

is explained by a decrease in mobility of macromolecules under load as a result of their orientation, which creates entropic difficulties for hydrolysis.

It is reasonable to expect similar effects of stresses on destructive processes of heterochain polysaccharides.

10.2 Effect of Natural Aging Duration on Some Fire Safety Characteristics of Members of Old and Ancient Timber Buildings and Structures

The variety of physical and chemical processes occurring in timber during its service does not allow highly accurate artificial reproduction of all the transformations occurring in it or predicting the pattern of property changes. To assess the impact of aging on the fire safety of timber building construction members, it is preferable to study timber specimens of existing old timber structures and architectural monuments experimentally. This approach requires exact knowledge of the service life of the object and the natural/climatic conditions of its location.

This is why our attention was drawn to timber specimens from existing old residential and other structures in the moderate climate region of Russia (Vologda, Kostroma, and other regions). Timber specimens in the form of saw cuts were taken from buildings situated in the villages of Demyanovo, Levino, Lyabzunka, and Semigory (Vologda Region) as well as in the villages of Nikitino and Shulevo (Kostroma Region).

The service life of the timber structures was 60–150 years according to the registered metrics. The structures were coniferous timber residential and nonresidential buildings, i.e., fir and pine (Figs. 10.3, 10.4, 10.5, and 10.6).

Timber specimens were sawed from the logs of the buildings' northern and southern parts free from decomposition, 1.5 m from the ground surface.

Fig. 10.3 Nonresidential timber structure (Levino vil.), fir, 90 years

Fig. 10.4 Nonresidential timber structure (Lyabzunka vil.), fir, 60 years

Fig. 10.5 Timber house (Semigory vil.), pine, 150 years

Fig. 10.6 Timber house (Nikitino vil.), pine, 130 years

Deciduous and coniferous specimens taken from old religious buildings were partially involved in studying the impact of natural timber aging on decomposition processes, and heat and fire resistance.

To get an idea of the specific specimens being studied, their density, ultimate composition, and content of the basic timber components were determined, and thermal analysis was performed.

We have already mentioned that timber density (volume weight) is an indicator of the macrostructure and influencing its properties. Many characteristics of material fire safety are related to density. Table 10.4 gives the average values of density ρ_{12} of the pine specimens studied.

The characteristic curve plotted according to these data (Fig. 10.7) has a complex nonlinear pattern, maximums and minimums. The maximum density values are observed in timber with a service life of about 100 and 330 years, while the minimum value is reached for pine with a useful life of 190–200 years.

This nonlinear variation of timber density due to long service life agrees with papers (Varfolomeyev et al. 1990; Pischik 2005). Density is nonuniformly distributed in different parts of timber structures oriented in different directions. Density is particularly high on the southern and eastern parts. Apparently, this is not haphazard. This may be a response to sunlight. Unfortunately, exact data on the biological age of the timber used for the timber buildings were lost. Religious buildings were usually made of pine 150–220 years old (Kisternaya and Kozlov 2007), while residential and business structures were 60–100 years old. Fir timber was more often used for business structures.

Table 10.4 Density of timber specimens with different service life

Item no.	Timber specimen, its source, year of construction	Service life, years	Density ρ_{12}, kg/m^3
1	Present-day pine, Vologda Region	–	440
2	Pine, Tolstoy house, 1830	180	410
3	Pine, Volkoostrov, Kizhi, Chapel of Peter and Paul	330	587
4	Pine, Church of Ipatyevsky Monastery, Kostroma, 1628	370	535
5	Pine, Saint George Cathedral, Shulevo vil., Kostroma Reg., 1898	112	North – 488 South – 537 East – 414 West – 426
6	Pine, Nikitino vil., Kostroma Reg., 1876	130	North – 505 East – 591 West – 561

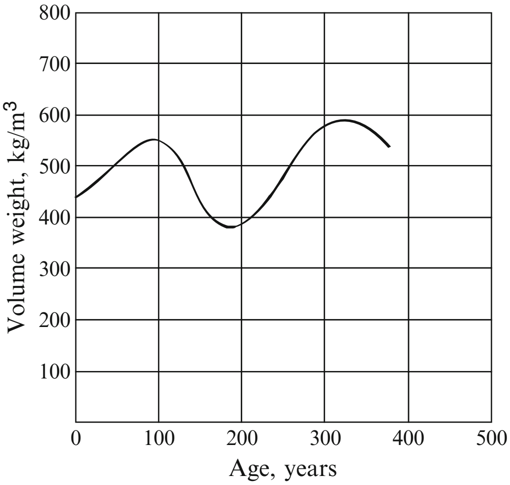

Fig. 10.7 Pine timber density ρ_{12} (volume weight) vs. service life

The dependence of destructive processes in timber on the where the samples were taken in relation direction (sunlight effect) can be judged by the results of chemical analysis (Table 10.5).

We used a simplified scheme of timber chemical analysis (Obolenskaya et al. 1991). The content of cellulose and lignin was assessed. The remaining part was a mixture of hemicelluloses and extractives.

The research results show that cellulose content decreases as service life increases to 150 years, while the lignin content increases (Table 10.5).

It can be seen that the southern part of the timber structure shows more significant changes than its northern part. Under approximately equal conditions, the percentage of cellulose in timber structural elements decreased by 13.9 % on the structure's southern part and by 9.1 % on the northern part over 150 years of service.

Table 10.5 Content of main chemical components of fir timber as a function of its service life

			Main chemical component content, %	
Item no.	Sample, source, service life years	Direction	Cellulose	Lignin
1	Present-day fir (Vologda Region)	–	54.5	25.4
2	Nonresidential timber structure (Lyabzunka vil.), fir, 60 years	North	55.6	25.6
		South	53.4	27.1
3	Nonresidential timber structure (Levino vil.), fir, 90 years	North	50.6	27.1
		South	49.0	28.2
4	Nonresidential timber structure (Demyanovo vil.), fir, 110 years	North	50.8	26.9
		South	48.6	28.1
5	Timber residential structure (Semigory vil.), fir, 150 years	North	49.5	27.6
		South	46.9	28.8

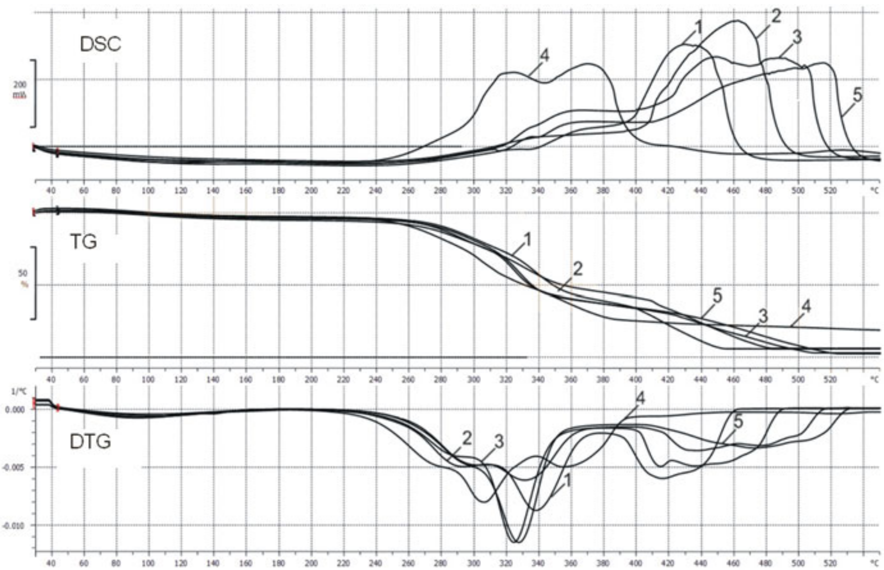

Fig. 10.8 *TG*, *DTG*, and *DSC* curves of oak specimens with different service life: *1* 1650, *2* 1901, *3* aged artificially by 80 years, *4* 1540, *5* present-day timber. Air medium, heating rate 20 °C/min

During aging, a significant role is played by thermo-oxidative timber decomposition reactions.

Therefore, important information on timber decomposition dynamics when it is heated in air can be obtained by thermal analysis methods. A TGA/DSC1 thermoanalytical system manufactured by Mettler Toledo (Switzerland) was used to study the patterns of thermo-oxidative decomposition of different timber species as well as the char residues. The set had a module for programmed calculations of kinetic parameters. Samples were prepared in the form of powder weighing 1.0–8.5 mg. Heating rate was 5–20 °C/min (Fig. 10.8).

All timber varieties are characterized by a low-temperature stage due by moisture and two main stages of specimen weight loss in the region of 240–400 and 400–540 °C. However, the position and maximum values of the characteristic points of TG, DTG, and DSC curves differ considerably for different timber species. An increase in heating rate causes the logical shift of the thermoanalytical curves to the higher-temperature region. Comparative analysis of the curves suggests that coniferous species begin decomposing earlier and faster than deciduous species when heated to 360–400 °C.

Thermo-oxidative decomposition of timber is a process involving significant heat release at all its main stages. This is confirmed by the exopeaks' presence on the DSC curves. Timber decomposition in the air is accompanied by charring. The greatest heat release during thermo-oxidative decomposition is related to the oxidation of the carbonized product at high temperatures.

Natural aging of timber structural elements causes a significant change in their thermal stability (Serkov et al. 2009; Aseeva et al. 2009).

Oak specimens taken from the boards of icons of the Trinity Monastery of St. Sergius (Moscow Region) were used to trace the impact of service life duration on thermo-oxidative timber decomposition (Fig. 10.8). We can actually see significant changes in thermo-oxidative stability of the oak specimens, which are particularly noticeable on the DSC and DTG curves. The longer the timber's service life, the greater the changes will be. All of the temperature indices decrease after natural aging of oak timber during a service life of more than 460 years: the starting temperature of decomposition, temperature of the maximum weight loss rate, etc. (Serkov et al. 2009).

An examination of thermoanalytical timber curves leads to the important conclusion that conditions favorable for timber decomposition, charring reactions, and oxidation of the charred product are created due to natural material aging during long-term service. This is most likely due to the increased lignin content caused by aging (a high-energy aromatic component of timber) and changes in porous timber structure.

The authors of paper (Sandu et al. 2003) observed a similar situation during thermal analysis of specimens of lime timber taken from frames and boards of old icons at Romanian monasteries. As the specimens' service life increased from 6 to 200 years, thermo-oxidative stability decreased, activation decomposition energy decreased, and the pre-exponential factor decreased by three orders compared to the reference lime tree specimen. However, timber with 99 years of service life was more stable than the reference specimen and the product more old. The effective activation energy of decomposition of this lime specimen was estimated in 105.2 kJ/mol and ln $Z = 20.8$ (the reference sample had values of 85.5 kJ/mol and 16.6, respectively).

Paper (Pokrovskaya et al. 2000) traced a particularly broad range by timber service life and its impact on thermal stability of timber structural elements. The authors had specimens of pine cut in 1990, 1991, 1880, 1790, 1752, 1690, 1612, 1576, and 1511. The specimens in the research conducted in 1990 corresponded to

Table 10.6 Influence of service life of timber structures on timber complete combustion heat

Item no.	Timber specimen, source, service life years	Element composition, %				
		C, %	H,%	O, %	Qn_e, kJ/g	Qn_r, kJ/g
1	Pine	52.14	5.91	41.95	19.6	19.1
2	Fir	52.22	6.04	41.74	18.9	19.25
3	Oak	50.40	5.77	43.43	18.7	18.2
4	Oak, monastery, 1650	47.03	7.25	45.72	18.0	18.3
5	Pine, Tolstoy house, 1830	49.38	3.88	46.74	15.2	15.52
6	Nonresidential timber building (Lyabzunka vil.), fir, 60 years, northern side	50.3	6.44	43.26	18.4	19.21
7	Nonresidential timber building (Levino vil.), fir, 90 years, northern side	48.3	7.11	44.6	18.15	18.6
8	Nonresidential timber building (Demyanovo vil.), fir, 110 years, northern side	46.7	8.2	45.1	19.8	20.3
9	Residential timber building (Semigory vil.), fir, 150 years, northern side	50.5	8.47	41.03	20.1	20.7
10	Timber structures of Saint George Cathedral, Shulevo vil. (year of construction – 1898), pine	45.9	8.15	45.95	18.3	18.9
11	Residential timber building, Nikitino vil. (year of construction 1876), pine	48.8	8.34	42.86	19.9	20.4

a service life up to 525 years. A cyclic nonlinear pattern of variation of weight loss values and kinetic parameters of the timber decomposition process was found. The minimums on the $E_{\text{eff}} = f(\tau)$ curves corresponded to timber structures with service life of about 100, 300, and 500 years; the maximums were in the regions of 200 and 400 years. The values of lg Z are changed almost synchronously. They increased by 2–5 orders at the maximum points. Timber is most vulnerable to destructive processes during the first 50–100 years of service. The cycles are repeated every 200 years.

During these periods, one should expect an increase in timber fire hazard. In the first place, it was necessary to determine the impact of natural aging of timber specimens on enthalpy of complete combustion. For this purpose, dry timber specimens with different service life were used. The lower heat of complete combustion values were determined experimentally using an IKA – calorimeter C 5000 – and were also calculated according to the element composition data by the Mendeleev equation. Table 10.6 presents the results.

As the service life of timber structures increases, the carbon content decreases, while hydrogen and oxygen contents increase proportional to each other. The exception is pine timber dating from 1830, where the hydrogen content decreased to

Table 10.7 Parameters of fir ignitability depending on timber structure service life

Item no.	Timber species, age	q_e, kW/m^2	τ_i, s	q^i_{cr}, kW/m^2	MLR$_{max}$, g/m$^2\cdot$s
1	Present-day fir (Vologda Region)	30	20	11.5	–
		40	7		–
		50	3		39.6
2	Nonresidential timber structure (Demyanovo vil.), fir, 110 years, southern side	30	26	13.2	–
		40	12		–
		50	6		31.9
3	Fir (residential building, Vologda Region, Semigory vil.), 150 years, southern side	30	21	12.5	–
		40	9		–
		50	4		35.7

3.88 %. The calculated and experimental assessment of the lower heat of complete combustion of specimens shows that the lower heat of complete combustion tends to increase as the timber's service life increases.

This is caused by a reduction in carbon content and an increase in hydrogen content in the element composition: hydrogen's contribution to complete combustion heat is four times larger than that of carbon. The observed effects fully agree with the results of an analysis of changes in timber chemical composition during aging.

The question of the effect of natural timber aging on such fire hazard properties as ignitability, mass burn-off rate, heat release rate, smoke generation capacity, and toxicity of combustion products is of interest.

Ignitability parameters of timber specimens were determined according to GOST 30402-96. The unit was provided with an additional device for recording mass loss during testing. It is found (Aseeva et al. 2009) that the delay time of ignition and the value of critical heat flux of specimen ignition increase as timber's volume mass (density) increases. These observations are in complete agreement with the thermal theory of ignitability of different materials.

The effect of duration of natural aging of fir timber constructions on the ignitability parameters is given in Table 10.7.

Table 10.7 shows that the ignition delay time of each timber specimen depends on the intensity of external heat flow. In identical testing conditions, fir timber with service life of 110 years shows higher values of τ_i compared to the reference sample and the specimen with service life of 150 years. The same trend is observed for critical ignition heat flow density q^i_{cr}. At the same time, the maximum mass loss rate of timber MLR$_{max}$ decreases accordingly at an external heat flow of 50 kW/m^2.

The impact of natural timber aging on flammability was also checked in severe conditions of exposure to the standard fire temperature regime when the average volume ambient temperature (T) at the process development stage increases according to the following equation:

$$T = 345\lg(8\tau + 1) + T_0,$$

where τ is the fire exposure duration, min, and T_0 is the initial temperature, °C.

Table 10.8 Impact of natural timber aging on flammability of timber structural members in a standard fire regime

Timber specimen, source	Service life, years	Time τ_{si}, min: s
Present-day fir	–	4 min 17 s
Nonresidential timber structure (Lyabzunka vil.), fir	60	4 min 30 s
Nonresidential timber structure (Levino vil.), fir	90	4 min 52 s
Nonresidential timber structure (Demyanovo vil.), fir, southern side	110	5 min 5 s
Fir, nonresidential structure, Vologda Region	150	5 min 2 s
Pine, present-day structure, Republic of Mariy El	2	3 min 73 s
Pine, nonresidential structure, Republic of Mariy El	12	3 min 59 s
Pine, nonresidential structure, Republic of Mariy El	48	4 min 17 s
Pine, nonresidential structure, Republic of Mariy El	59	4 min 22 s
Pine, nonresidential structure, Republic of Mariy El	88	4 min 31 s
Pine, nonresidential structure, Republic of Mariy El	113 years	4 min 49 s

For this purpose, a small-scale firing furnace was used, where the standard temperature–time conditions were provided by a special gas burner with adjustable propane gas supply. Thermocouple sensors allowed automated recording of the average volume temperature in the furnace as well as the specimen's surface and inner temperature. Vertically oriented timber specimens were $150 \times 150 \times 20$ mm. In this case, the self-ignition delay time of the timber specimens from the time the specimens were placed in the fire furnace was recorded (Table 10.8).

The results obtained for fir timber tests in standard fire regime agree with the above-mentioned nonlinear trend of changes in timber flammability as the service life of timber structures increases. At the same time, this trend was not revealed for pine specimens, although the general upward trend in τ_{si} with an increase of timber structures' service life to 113 has a similar pattern. Pine timber in standard fire regime is a bit more prone to ignition compared to fir.

Combustion is first of all a physicochemical process of oxidation of any substance. Timber chemistry changes during long-term natural aging will affect the materials' fire safety parameters directly related to the chemistry of this process. Smoke generation capacity is also one of these indices.

Figure 10.9 shows the experimental results of assessing the smoke generation capacity of pine timber depending on duration of natural aging of timber structures. Smoke generation capacity was determined by the standard methods according to GOST 12.1.044-89 in decomposition and smoldering conditions at external radiation heat flow of 20 kW/m^2.

The smoke generation capacity of timber structural elements in old constructions changes nonlinearly as service life increases.

Figure 10.9 shows that the minimum smoke generation capacity is for pine timber structures with service life of 100–150 and 300–330 years. This result generally agrees with the above-mentioned pattern of variation of other timber properties during natural aging.

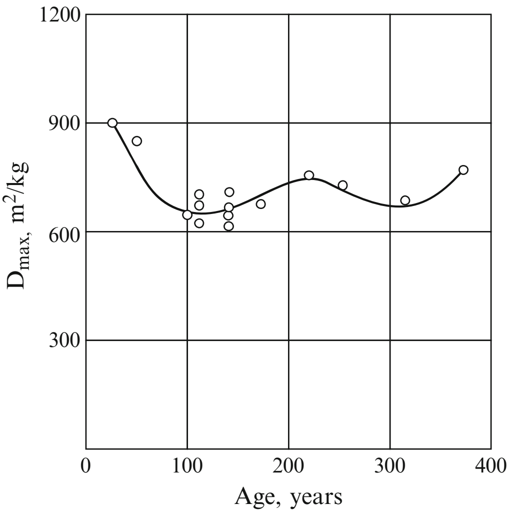

Fig. 10.9 Pine timber smoke generation capacity (D_{max}) vs. service life of timber structures $q_e = 20$ kW/m^2

The research results as a whole lead to the conclusion that the processes occurring during natural timber aging are rather slow. They depend on timber variety and local climatic conditions of timber structure service and are due to a complex combination of thermal, photo-oxidative, and hydrolytic reactions of timber decomposition. As a result of the change in macrostructure and chemical composition of timber materials, all of their properties change, including fire safety characteristics. For a timber building with a very long service life, the observed transformations are nonlinear in time, which affect the materials' fire safety.

10.3 Charring Parameters and Physical Properties of Char Formed During Fire Action on Old Timber Building Elements

Timber charring is one of the important factors determining fire resistance of timber structures and constructions. Timber charring in various fire situations is still a subject of numerous studies. Timber charring parameters during a fire and properties of the charred layer are of great practical interest. This interest is due not only to the need for initial data for engineering estimation and design of building structures with a standardized fire resistance and fire safety level and for predicting the behavior of different timber species in case of fire. By analyzing the charring parameters and properties of the charred layer, experts can determine when the fire started and its duration, seat of fire in a room, and establish the cause and probability of arson.

The process of timber charring under fire exposure is usually characterized by such parameters as charring rate, thickness (depth), and shrinkage of the charred

layer and less often by mass loss rate. Physical properties of the charred layer are studied from various aspects. Its thermophysical, heat-insulating properties, porous structure, permeability, electrical resistance, etc., are of interest.

Charring parameters of timber and materials on its basis depend on conditions of fire exposure. The conditions of external heat exposure and fire determine the conditions of material heating, and its pyrolysis and charring rates. Different standard methods are used to compare the behavior of various timber species and timber-based materials by charring parameters. In particular, these include methods implementing the following regimes: standard temperature–time fire, impact of external radiative heat flow of constant density, and environmental impact at constant temperature.

This section presents the experimental results of studying the effect of natural aging of elements of timber structures in old buildings on charring parameters and properties of the charred surface layer formed in 20 min during a standard fire. For this purpose, we used the above-mentioned small-scale furnace and specimen sizes. Charring rate and thickness (depth) of the charred layer for the whole period of fire exposure were calculated as the mean arithmetic values of three repeated tests of each type of specimen. Timber specimen charring rate in a standard fire after self-ignition increased to the maximum value and then slowed down. The maximum values of charring rate were used for comparison.

Table 10.9 gives the charring parameters and density of charred layers formed on the surface of pine and fir timber specimens with different service life. The char layer surface temperature corresponding to the maximum charring rate is also given here.

A comparison of the values of charring rate as well as the thickness of the charred layer formed in a standard fire and the effect of radiation heat flow of constant density shows that the timber charring process accelerates in more severe conditions of thermal exposure. As the service life of timber structures increases to 150 years, natural aging of structural elements also causes an increase in the charring rate in standard fire conditions (Fig. 10.10).

The observed rise of charring rate and char layer thickness is mainly related to the increased lignin content in the timber due to natural material aging. Density of char layers on the surface of fir timber specimens is virtually identical and does not depend on aging duration. However, it decreases in pine structures with 150 years of service life (from 256 to 212 kg/m^3). This indicates in increase in char structure porosity. The surface of charred layers in a standard fire incandesces to almost 800 °C.

The effect of natural timber aging on some characteristics of its reaction to fire was studied for coniferous species only (fir, pine). It is also important to determine the effect of aging on behavior during fire and fire safety of deciduous timber varieties. Therefore, it seemed reasonable to conduct a comparative study of the change in the main fire safety characteristics of coniferous and deciduous timber species subjected to accelerated artificial aging.

Table 10.9 Effect of natural timber aging on charring parameters and density of charred layers

Specimen, source, service life	δ_C, mm	V, m/min	ρ_C, kg/m^3	T_s, °C	k, W/m K	a, m^2/s	$k\rho c$, kJ^2/m^{4}K^{2}s
Fir, nonresidential timber structure (Lyabzunka vil.), 60 years	22	1.4	223	796	0.37	0.0010	0.128
Fir, nonresidential timber structure (Levino vil.), 90 years	24	1.55	214	805	0.30	0.00089	0.10
Fir, nonresidential timber structure, (Demyanovo vil.), 110 years	26	1.63	213	816	0.26	0.00078	0.086
Fir, nonresidential structure, Vologda Region, 150 years	27	1.72	212	812	0.20	0.0006	0.066
Pine, nonresidential structure, Republic of Mariy El, 2 years	19	1.0	256	731	0.33	0.00082	0.131
Pine, nonresidential structure, Republic of Mariy El, 12 years	24	1.1	254	736	0.31	0.00078	0.122
[a]Pine, 12 years, $q_y = 20$ kW/m^2	19	0.95	278	558	0.10	0.00056	0.043
Pine, 48 years	25	1.25	249	738	0.27	0.00069	0.104
Pine, 59 years	26	1.3	242	744	0.24	0.00063	0.09
Pine, 88 years	25	1.34	237	749	0.23	0.00062	0.085
[a]Pine, 88 years, $q_e = 20$ kW/m^2	20	1.0	256	570	0.07	0.00017	0.027
Pine, 113 years	30	1.5	217	822	0.24	0.0007	0.081
Pine, nonresidential structure, Vologda Region, 150 years	26	1.5	212	812	0.20	0.0006	0.066

[a]Timber specimens were subjected to an external radiation heat flow of constant density $q_e = 20$ kW/m^2 for 20 min as per GOST 30402-96

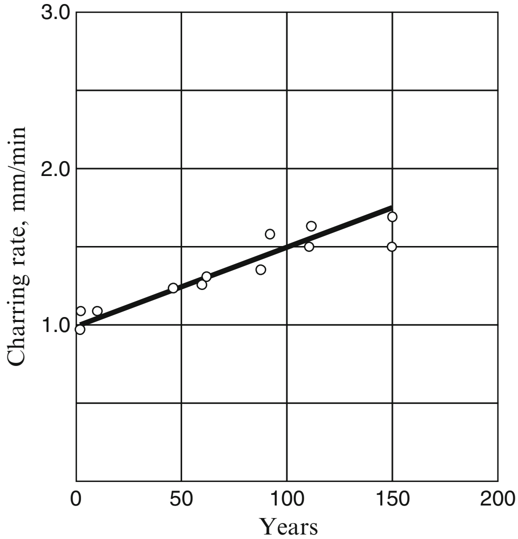

Fig. 10.10 Effect of natural aging of timber structures on timber charring rate (fir, pine) in a standard fire

10.4 Biodegradation of Timber and Complex Bio-, Moisture, and Fire Protection of Constructional Timber Materials

Fungal infections and insects play an important role in damaging timber structures. Timber-destroying fungi are divided into two large groups according to their physiological effect: destructive, destroying cellulose, and corrosive, attacking lignin.

Cellulose-destroying fungi cause brown rot, and those destroying lignin cause white rot. A feature of the enzymatic system of white rot microorganisms is also its activity toward partial or full destruction of polysaccharides.

Destructive brown rots caused by several types of household fungi have been detected in long-used wooden architectural monuments of the Russian North. They include a real household fungus Serpula lacrymans, the membranous fungus Coniophora puteana, white fungi Coriolellus sinuosus and Fibroporia vaillantii (Fr.), and the agaric fungus Paxillus panuoides Fr. (Kisternaya and Kozlov 2007). Timber affected by fungi first acquires a brown color, and deep lengthwise and crosswise cracks appear in it. Then the rot breaks down along the cracks into small prism-like pieces that are easily converted into brown powder.

Under natural conditions, bio-destroyers of timber like white rot mainly affect the wood of living plants. Insects that bring fungi to the conductive tissues of trees serve as fungi agents. The sequence of anatomical and chemical changes in timber of various species under the influence of white rot fungi was studied using light microscopy (Malysheva 2004). It was established that, depending on the timber variety and type of fungi, either selective delignification of timber or simultaneous destruction of lignin and the carbohydrate part of timber (hemicellulose and

cellulose) occurs. Timber damage often started from wood rays, from where white rot hyphae, via bordered pits, penetrated into tracheids and elongated thick-walled cells, and completely destroyed the main components of sheathing tissue.

Furthermore, internal layer S_3 of sheathing tissue with increased hemicelluloses content was the first to be affected. Lignin-enriched middle lamellas were the last to be destroyed, which is why the cells preserved their form for a long time. This type of simultaneous deterioration of the lignin–carbohydrate complex was accompanied by cracking of the timber into small prism-like pieces resembling brown rot.

The process of selective delignification of sheathing tissue of timber under the action of white rot fungi (Phanerochaete sanguinea) was more complicated and diversified. In some cases, delignification started from internal layer S_3 and ended with middle lamella. In other cases, removal of lignin from the same cells occurred simultaneously and in opposite directions: from external layer S_1 to middle lamella and toward it from internal layer S_3. In this case, lignin from layer S_2 was the last to be removed. The cells separated from each other took the form of nearly regular rings.

The varieties of fungi infecting timber are numerous. A detailed mechanism of their destructive action has not been clarified to date.

It has been established that fungal activity depends on ambient temperature, moisture content in the timber, and species and type of the timber itself (Zabel and Morrell 1992). For this reason, the influence of climatic conditions of the region where woody plants grow or wooden structures are used is most pronounced. High destructive activity of fungi is observed at ambient temperatures above 5 °C and moisture content in timber over 20–25 %. Under such conditions, timber infected by fungi decays very quickly, within several years, as temperature and sufficient moisture content promote fast development, growth, and multiplication of fungi. Destruction of timber by fungi slows down considerably or ceases if the ambient temperature falls below 2 °C and below zero.

An increase in the ambient temperature beyond 35–45 °C, in turn, favors the fermentation activity of fungi.

It is assumed (Kisternaya and Kozlov 2007; Zabel and Morrell 1992; Venalainen and Harju 2004) that the mechanism of the destructive effect of fungi is connected with their participation in two processes: (1) free radical formation, initiating oxidative breakdown of polysaccharide molecules, and (2) acid agent formation (like acid of sugar), causing hydrolysis of timber components. In both processes, a large role is played by ferments produced by fungi, which are biocatalysts of destructive reactions.

The importance of the hydrolytic line of timber biodegradation confirms the influence of temperature and moisture conditions on the destructive effect of fungi, and its dependence on species and morphological structure, and timber pore space. Data on the influence of the content of phenol compounds from the stilbene group in extractives from sap and pine trunkwood favor the radical mechanism of timber biodegradation (Venalainen and Harju 2004). A higher concentration of phenols, which are natural inhibitors of radical oxidizing reactions of various substances, explains the higher natural resistance of trunkwood to the destructive effect of fungi.

The destructive effect of fungi is typically judged according to loss of timber weight for a specific period of fungal attack (Kisternaya and Kozlov 2007). The reciprocal value of this weight loss serves as a measure for timber's resistance to destruction by fungi (Venalainen and Harju 2004).

Based on an analysis of the change in the content of main chemical components of timber and ultimate composition of the organic part as a result of biodegradation, the following stoichiometric equations have been proposed for the reactions (Soloviev 2004):

(a) Corrosion (white rot fungi):

$$4C_6H_9O_4 + 25O_2 \rightarrow 24CO_2 + 18H_2O + 11.53 \times 10^3\text{kJ}.$$

(b) Destruction (brown rot fungi):

$$C_6H_{10}O_5 + 6O_2 \rightarrow 6CO_2 + 5H_2O + 2.83 \times 10^3\text{kJ}$$
$$C_5H_8O_4 + 5O_2 \rightarrow 5CO_2 + 4H_2O + 2.34 \times 10^3\text{kJ}$$

In the author's opinion (Soloviev 2004), the foregoing equations show the connection between timber weight loss and the amount of absorbed oxygen; products formed, namely, carbon dioxide and water; and emitted heat.

The kinetic approach to determining the weight loss rate during timber biodegradation via its connection with the rate (intensity) of oxygen absorption or carbon dioxide emission opens wider possibilities for evaluating the functional role and activity of timber-destroying fungi.

Natural resistance of timber to rotting, all other conditions being equal, depends on species and timber variety. The trunkwood of Scotch pine and Siberian larch, oak, and ash is considered most resistant to biodeterioration (GOST 20022.2-80). Fir, silver fir, and beech timber are moderately resistant. Sensitive timber includes elm, maple, and birch. Lime tree, alder, and aspen timber are nonresistant materials. Not only the physical structure of timber and the ratio between sap and trunk parts but also the chemical composition of timber are of importance.

It should be noted that the most intensive destruction of wooden structures by fungi occurs in places where they make contact with the soil.

In research paper (Varfolomeev et al. 2004), the influence of duration of service life of pile foundation timber on its being attacked by wood-destroying fungi in the soil aeration zone was analyzed; strength properties of pile shafts were determined for various extents of fungal attack. Fragments of piles of as-built dimensions (diameter 24 cm) were cut from sites located 0.3 m above and 0.4 m below the ground surface. The service life period of pile foundations of timber houses (Archangelsk) being analyzed was from 10 to 87 years. It was established that the content of timber affected by fungi in cross section of the samples (G, %), depending on the service period (τ, years), can be represented by the equation:

$$G = 1.104\tau - 9.743, \%.$$

The correlation factor R is 0.73.

The healthy part of the trunkwood of piles without defects and not affected by fungi preserved its strength properties after long-term usage.

Dependence of the compressive strength of piles along the grain from the area of fungal attack of the cross section of the samples (G, %) corresponds to the following equation with correlation factor 0.84:

$$\sigma_{\text{compr}} = 11.553\text{–}0.106\ \text{G, MPa.}$$

Taking into account the largest stress acting in the shaft of the pile foundations of timber houses (3.65 MPa), the authors (Varfolomeev et al. 2004) distinguished three stages of pile usage: (1) guaranteed safe usage stage, fungal attack up to 13 % (the compressive strength of timber along the grain is higher than the standard value); (2) safe usage stage, fungal attack up to 59 % of the cross section (the actual compressive strength of the samples along the grain is higher or corresponds to the largest value of stresses acting in the pile shaft); and (3) hazardous usage stage when over 59 % of the cross section has deteriorated and pile failure is possible.

The only really effective means for protecting timber structures in contact with ground against biodegradation is careful moisture proofing.

Insects of the wood-fretter family cause a great deal of damage to timber building structures (Kisternaya and Kozlov 2007). The furniture beetle (Hadrobregmus pertinax L.) and northern wood-fretter (Hadrobregmus confuses Kr.) are active in unheated timber structures in the European part of Russia. Their optimal development is observed at a moisture content in coniferous wood above 18–19 % and temperature about 25 °C. At temperatures beyond 48 °C, they die out at all stages of their existence.

The furniture beetle lives mainly in coniferous wood in places exposed to frost action. These are attic floor elements, logs of lower crowns, damp places under window sills, rough timber boarding, etc. The northern wood-fretter damages coniferous wood only. It is detected in crown logs at any height. The grubs cause major damage to timber.

Controlling these pests is a more complicated task compared to wood-destroying fungi, since beetles and their grubs are capable of functioning in timber with low moisture content (10–12 %). External damage and inlet openings in timber made by the beetles are small and invisible.

Various methods were applied historically, most often chemical preservation methods with the use of different antiseptics and disinfectants, in order to protect timber structures against fungal infection and the activity of insect pests. A large number of chemical protection agents were developed and tested (GOST 20022.2-80). The experience accumulated over many years of using various agents showed their benefits and drawbacks.

In Russia, for example, effective antiseptics based on pentachlorophenol or its phenol sodium (PBB-211, PZS) were widely used in order to protect timber architectural monuments against biodegradation. Deep treatment of timber with PBB-211 by the panel method caused additional internal stresses and the appearance and expansion of cracks in log structures. Twenty-four years after treatment of

timber structures of Pokrovsky Church on Kizhi Island, the level of chlorophenol content in air in close proximity to the treated walls exceeded MPC (0.01 mg/m^3) by several times (Kisternaya and Kozlov 2007). From 1984 in Russia (GOST 20022.2-80) and from the beginning of the 1990s in the EU, agents based on pentachlorophenol have been excluded from the List of Authorized Bioprotective Elements for timber residential and public buildings due to the potential formation of highly toxic dioxins.

For reasons of environmental safety, a similar situation has occurred with the use of very effective antiseptics and insecticides based on compounds of chromium, copper, and arsenic (CCA). In these agents, copper played the role of fungicide, arsenic served as a fungicide and insecticide, and chromium was the fixator, contributing to the formation of insoluble compound forms, and, thus solving the problem of environmental emissions of toxic substances from timber.

However in Europe, Directive 2003/2/EC limited sales and use of arsenic compounds, including CCA compounds, for treating the structures of timber residential and public buildings with a high degree of contact between materials and people. A similar practice was subsequently adopted in the USA and Australia.

Many timber preservatives displaying functions of fungicides and insecticides proposed instead of CCA (e.g., complex of copper compounds with quaternary ammonium bases or with cyclic nitrogen-containing substances) cause ferrous metal corrosion.

The preservatives that protect timber against bio-destroyers, enhance fire safety of timber structures, and protect against the harmful effect of moisture are of primary concern. The problem of developing effective protective agents with similar multiple functions is of immediate interest not only from the point of view of preserving historical monuments of timber architecture. Its solution is also important for increasing the durability of timber structures of present-day constructional members.

Work on developing a multipurpose fire-, bio-, and moisture-protective compound for timber, and the detailed study of its effect, was carried out in the SFSA bay leadership of Prof. E.N. Pokrovskaya (Kobelev 2012). The prospects for using "soft" surface modification of timber with organic phosphorus and silicon compounds for this purpose were demonstrated earlier (Pokrovskaya 2003).

It is known that the condition and properties of surface layers of timber are responsible for the decorative and many other important usage parameters of timber products, in particular, hardness, durability, surface heat conductivity, resistance to the effects of atmospheric factors and aggressive media, etc.

The Fokkos compound has been developed from the principle of chemical interaction of surface layers of timber with reactive groups of organic phosphorus and silicon compounds (Kobelev 2012).

The compound's main components are dimethyl phosphite and oligomeric ethylhydrid siloxane. The formation of strong covalent links of these compounds with main timber components was proved by various research methods. Soft surface modification of pine timber as a result of treatment with Fokkos compound considerably increased the biostability of the material, halved the moisture and

water absorption of the samples, and increased the fire-protective characteristics of timber. The properties were assessed for all factors using standard methods accepted for determining biostability, moisture, and water absorption of timber and characteristics of its reaction to fire.

Compared to the known fire- and bio-protective compounds for timber (Latic-B, Attic, BB-11, Texturol-Quattro, etc.) that often require application of additional waterproof protective paint coatings, Fokkos compound is a more efficient, cost-effective compound. Much less of it is needed to achieve the necessary protection level. Tests of modified timber samples under laboratory conditions have shown the high, 100 %, biocidal activity of Fokkos compound against both destructive fungi (Coniophora puteana) and mold fungi causing timber corrosion (Penicillium biforme, Aspergillus niger).

Tests under in tropical conditions of Vietnam confirmed these results and also showed the high efficiency of the developed method for protecting timber against termite attacks (Kobelev 2012).

A detailed study of the fire-protective action of Fokkos compound was carried out not only according to the standard method (GOST R 53292-2009) adopted in Russia for estimating the effectiveness of fire protection means. Important fire safety data, such as flammability, flame spread, smoke generation ability, and toxicity of combustion products, have been determined. It has been established that this compound provides fire rating group I (mass loss on combustion less than 9 %). Timber from the group of materials that quickly spread flame ($I_{RP} = 60$) moves to the slowly spreading group (index $I_{RP} = 1.2$). In practice, due to intensive char formation, flame spreading on the sample surface stops immediately. Surface modification with Fokkos compound increases timber resistance to combustion on exposure to external radiation heat flow. Material from highly ignitability group B3 moves to moderately inflammable group B2. Critical heat flow of combustion increases from 12.5 kW/m^2 for the initial timber up to 20 kW/m^2 after surface modification of the samples. Smoke generation ability and toxicity of combustion products have been determined in the most hazardous regime of smoldering timber samples exposed to external radiation heat flow within the interval of 10–35 kW/m^2. Treating timber with Fokkos compound reduces smoke generation by almost 3.5 times and moves the material from group D3 with high smoke generation ability to group D2 with moderate smoke generation ability. A decreasing rate of toxic carbon monoxide formation is observed.

Unlike the initial timber, the surface-modified samples exposed to fire form uniform fine-pored char (average pore diameter is 2.3 Nm) with greater specific surface.

X-ray fluorescence analysis of the char showed considerable phosphorus and silicon content in the carbonized structure (2.6 and 2.1 %, respectively).

Based on the results of standard accelerated tests of timber samples in a climatic chamber in air with regulated relative humidity and temperature, it was concluded that the bio-moisture- and fire-protective effect of treating timber with Fokkos compound may be preserved for up to 20 years when the material is used under normal conditions.

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